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MICRO-SR-XRF STUDIES FOR ARCHAEOLOGICAL GOLD IDENTIFICATION – THE CASE OF CARPATHIAN GOLD AND OF ROMANIAN MUSEAL OBJECTS

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In the determination of the provenance of gold in archaeological artifacts, trace elements are more significant than the main components. Several minute fragments of natural Carpathian gold - placer and primary – and some very small (few milligram) fragments of archaeological items were studied using micro Synchrotron Radiation X-Ray Fluorescence (micro SR-XRF) at the BESSY Synchrotron Facility in Berlin, Germany. The goal of the study was to identify the trace elements characterizing Carpathian gold, looking especially at Sn, Sb, Pb and Te, and to determine if the gold in the archaeological items is native or refined. Applications to the authentication and provenance of nine Dacian gold bracelets, koson coins and two Bronze Age items are presented.

Keywords: *Micro SR-XRF, ED-XRF, Gold.*

INTRODUCTION

Romanian museums have remarkable archaeological gold objects, especially from the Bronze Age (2000-800 BC) and the Dacian period (400 BC-100 AD). The key problem for the archaeologist is to know if the gold was local (from the Carpathians) or "imported" from other sources (e.g. the Balkans or Anatolia).

Trace elements analysis is of major significance in the assignation of the provenance of archaeological artifacts, compared to other components. For gold, the most promising elements are the Platinum Group Elements (PGE), Sn, Te, Sb, Hg, Pb [1]. To help Romanian archaeologists in the authentication and provenance studies on ancient gold artifacts (jewelry and coins) found on Romanian territory [2], the very possible use of Carpathian gold must be considered and demonstrated. The goal of this study is to verify if

Transylvanian (Carpathian) gold was used to manufacture some Romanian archaeological objects. This is realized by using information related to trace elements: Sb, Te, Pb – recognized fingerprints for Carpathian mines, and Sn, characteristic for the panned, riverbed (alluvial) gold. To solve these issues, we measured samples from various Transylvanian mines and rivers - grains, nuggets, fine gold "sand" - and some very small (few milligram) fragments of archaeological objects: koson gold coins - staters, two fragments of an Early Bronze Age hair ring from the Tauteu treasure and a Late Bronze Age Vulchitrun disk. Another scope of this Synchrotron Radiation X-Ray Fluorescence (SR-XRF) experiment was to obtain the elemental characterization (Au, Ag and Cu content) of representative Transylvanian gold mines, subject of interest for the assignment of any other archaeological artifacts to one of the Central European gold sources.

EXPERIMENTAL

During the experiment, point spectra for 22 natural gold samples from Transylvania and 10 sub-millimeter size samples from archaeological objects were acquired at 34 keV excitation energy, using a spatially resolved SR-XRF set-up mounted for analyses at the hard X-ray beam line – BAM-line at BESSY [3]. The beam was focused to a beam size of 100×100 μm^2. The gold samples were mounted in air in a special frame for passe-partouts on a motorized xyz stage at an angle of 45° to the X-ray beam. Fluorescence signals were collected for 300 s each by a Silicon Drift Detector (SDD) detector covered by a polyethylene filter for protection against visible light. Data analysis was performed by means of the AXIL software package [4]. A video system and a long distance microscope allow to observe and to select the analytical points on the samples. Relative elemental concentrations are determined using a procedure based on different metallic standards.

RESULTS AND DISCUSSION

A summary for the characterization of Transylvanian native gold is the following:

- High (8 - 30%) Ag amounts and low (0.2 - 1%) Cu amounts;
- Placer deposits (Valea Oltului, Stanija, Valea Pianului) contain as fingerprint Sn (150-300 ppm) – most probably from river bed cassiterite (fig.1);
- Primary deposits present as fingerprints Te (200-2000 ppm), Sb (150-300 ppm) - however, the samples are very inhomogeneous (fig.2);
- Sacaramb primary deposit contains Te = 0,25%, Sb (500 ppm), but also Sn (200 ppm);
- Fizesti primary deposit presents a big amount of Pb = 1%, Sb (350 ppm), traces of Te and also Sn.

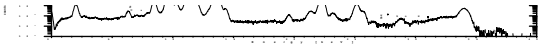

Figure 1: SR-XRF spectrum for alluvial gold 13-230.

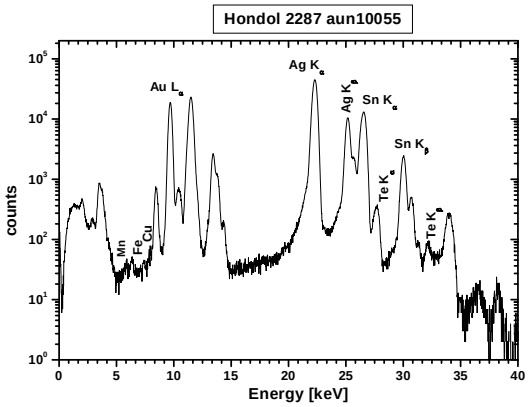

Figure 2: SR-XRF spectrum for Hondol 2287.

Many isolated pieces or large treasures of ancient gold coins (staters) were discovered in Romania, especially around Sarmizegetusa – the capital of Dacia [5]. The coins analyzed in this work (6 pieces) come from the recently discovered treasure (around 1000 kosons) at Târsa-Luncani [6]. This quaint type of coins is usually considered the only kind of gold coins issued by the Dacians. The strangeness of these coins consists in their Roman iconography.The obverse - an eagle standing left on a scepter holding a wreath in one claw - is inspired by the silver denarii issued by O. Pomponius Rufus; while the reverse - three togate male figures advancing left, the first and third of which carry an axe on their left shoulder - seems to be inspired by a silver denarius issued in 54 BC by M. Junius Brutus. The controversies around these coins are connected with the significance of the inscription, the place of mint and the issuer. There are 2 main types of koson coins: with and without monogram, undeciphered up to date. The study intended to determine whether the gold used for the koson coins is native or refined.

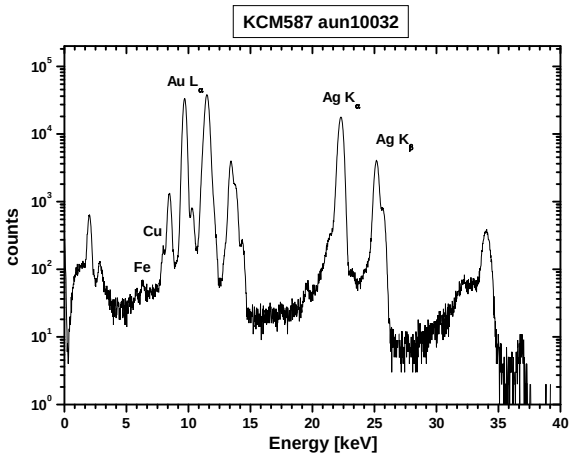

Figure 3: SR-XRF spectrum for KCM587 koson with monogram.

This study shows that the type "with monogram" is made from refined (more than 97%) gold with no Sb, Te or Sn traces (re-melted gold)(Figure 3), and the type "without monogram" is manufactured from native alluvial gold, partially combined with primary Transylvanian gold (Sn and Sb traces detected) (see Figure 4). For a comparison, the Greek "pseudolysimachus" type staters (contemporary with "kosons") are made of refined re-melted gold (no Sn, Sb, Te presence) (Figure 5).

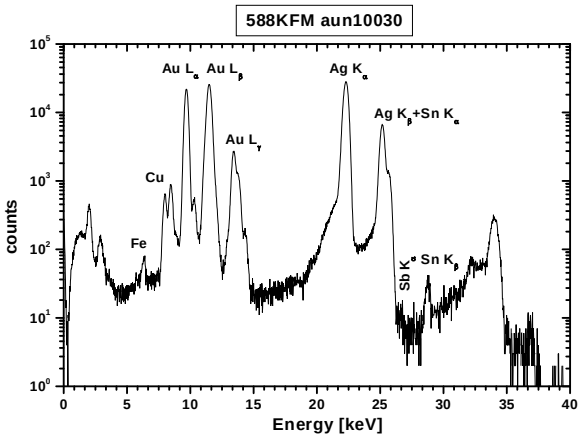

Figure 4: SR-XRF spectrum for 588 KFM koson without monogram.

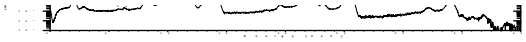

Figure 5: SR-XRF spectrum for Tomis 581.

Concerning the Early Bronze Age hair ring from the Tauteu hoard and the Late Bronze Age Vulchitrun disk [7] we found that both are made of alluvial gold (Figures 6, 7).

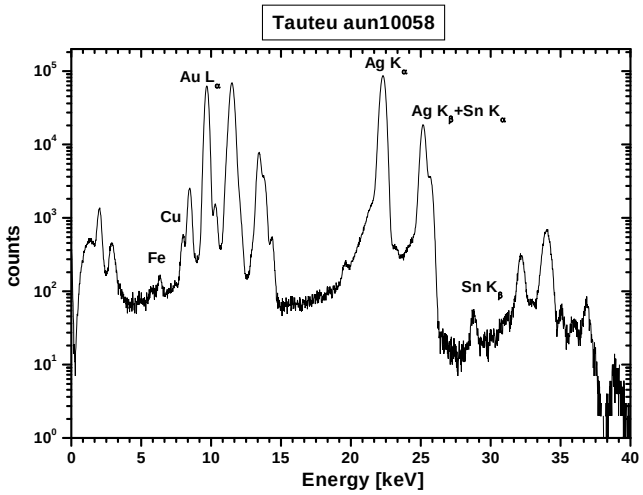

Figure 6: SR-XRF spectrum for Tauteu.

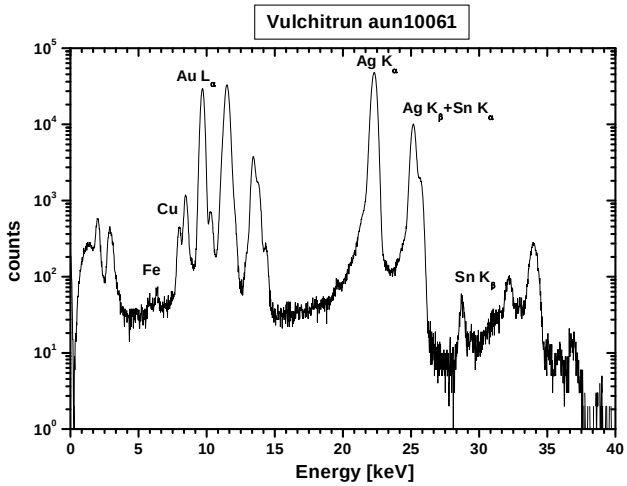

Figure 7: SR-XRF spectrum for Vulchitrun.

A spectacular application of the micro-SR-XRF studies on native gold was the one of authentication of some recovered heritage artifacts: nine Dacian gold bracelets belonging to the National Museum of History of Romania, Bucharest. The Dacian multi-spiraled gold bracelets they belong to the classical period of the Dacian civilization (2nd century BC - 1st century AD). The bracelets were recovered from the international market of antiquities through a common effort undertaken by Romanian and German authorities. The bracelets contain 5 – 7 spirals and weigh 800 to 1200 g each. They are 10 to 12 cm in diameter, adorned with stylized palm leaves and zoomorphic protomes at both ends. In order to confirm the authenticity of the bracelets, the analysis of the gold alloy from which they were made was strongly requested. The conditions imposed by the Romanian authorities were: local analyses (in Romania), no sampling (even for LA-ICP-MS!), no nuclear activation. Therefore, the compositional analysis of the bracelets was performed in early spring 2007, by X-Ray Fluorescence at Horia Hulubei National Institute of Nuclear Physics and Engineering, Bucharest, using ^{241}Am (30 mCi) and ^{238}Pu (10 mCi) radioactive sources, and a HPGe detector (Figure 8). The compositional results are presented in Table 1 (average of three measuring points). Other elements were present in traces: tin – from cassiterite – fingerprint for placer/panned gold; antimony – from jamesonite ($Pb_4FeSb_6S_{14}$), stephanite (Ag_5SbS_4); Ca-rich soil traces in cracks - proving that the bracelets had been buried for a long period of time. Another notable aspect is the relatively inhomogeneous composition of the bracelets. Earlier results on some items from this set have been published in [8].

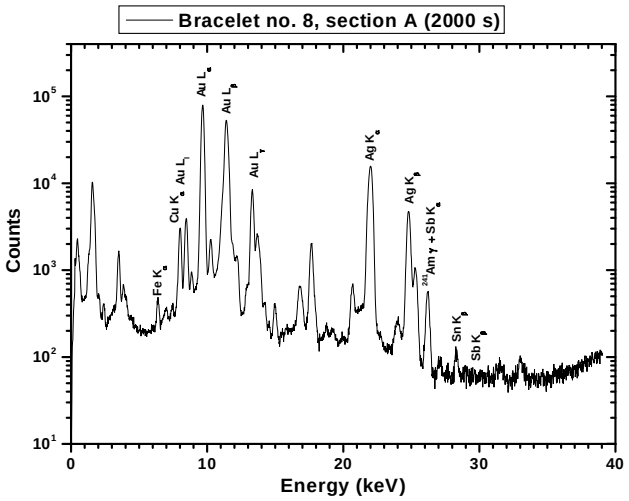

Figure 8: XRF spectrum for Dacian bracelet no.8.

Table 1: Gold, copper and silver composition (in % weight) for the set of 9 Dacian bracelets.

Bracelet no.	Au [%]	Cu [%]	Ag [%]
1	89.85	0.65	9.50
2	78.20	1.50	20.30
3	82.40	1.40	16.20
4	91.50	0.40	8.10
5	92.80	0.30	6.90
6	92.00	0.90	7.10
7	92.90	0.75	6.35
8	85.00	2.10	12.80
9	87.10	0.65	12.25

Comparing the XRF results on bracelets with the micro SR-XRF results on Transylvanian gold samples, the conclusion was that the bracelets were made from native Carpathian gold (panned mixed with primary) and manufactured with a primitive metallurgy, without refining of the native gold. Our results support strongly the stylistic arguments regarding the authenticity of the bracelets.

CONCLUSIONS

As a general conclusion of this study, both analytical methods employed- micro SR-XRF and ED-XRF – proved their usefulness in authentication of ancient gold artifacts. Due to its excellent performance regarding the detection limits, its non-destructive character and good lateral resolution, micro SR-XRF is the perfect choice for analysis in the case when minute samples are available for elemental analysis. However, in the case when neither sampling is allowed - due to the intrinsic value of the artifact, or the transportation of gold objects to an accelerator possible, in-situ (museum) ED-XRF measurements can be used as

a satisfactory alternative to investigate such precious objects. The study also shows the suitability of SR-XRF for geological studies of native gold.

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